reaction **8a** $\rightleftharpoons$ **8b** $\rightleftharpoons$ **8c** $\rightleftharpoons$ **8d** at 6 temperatures from 26 to 170 °C. In all cases, the position of equilibrium was approached from at least two initial mixtures of isomers with sufficiently different isomer compositions (for **1a** $\rightleftharpoons$ **1b**, for example, pure **1a**, pure **1b**, and a 1:1 mixture of these forms were used). The values of the thermodynamic parameters were evaluated by linear least-squares treatments of ln K vs. T^{-1}.

Registry No. **1a**, 592-57-4; **1b**, 628-41-1; **2a**, 30979-68-1; **2b**, 2886-59-1; **2c**, 2161-90-2; **3a**, 98677-91-9; **3b**, 28495-27-4; **3c**, 28495-28-5; **4a**, 98677-92-0; **4b**, 98677-93-1; **4c**, 98677-94-2; **6a**, 98677-95-3; **6d**, 98677-96-4; **7a**, 98677-97-5; **7b**, 13697-84-2; **7c**, 2161-93-5; **7d**, 2773-58-2; **8a**, 98677-98-6; **8b**, 53922-67-1; **8c**, 69697-78-5; **8d**, 69697-81-0; *i*-PrOH, 67-63-0; 2-cyclohexen-1-one dimethyl acetal, 1728-18-3; 3-pentanol, 584-02-1.

Onium Ions. 33. (Trimethylsilyl)- and [(Trimethylsilyl)methyl]oxonium and -halonium Ions[1]

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A series of (trimethylsilyl)- and [(trimethylsilyl)methyl]oxonium and -halonium ions were prepared under stable ion conditions by alkylating the corresponding trialkylsilyl ethers or halides. The ions were studied by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The trend of observed ^{13}C NMR shift deshielding effects indicates little charge delocalization occurring due to the α- or β-trialkylsilyl substituents as compared with parent alkyloxonium and -halonium ions. The [(trimethylsilyl)methyl]- and (trimethylsilyl)oxonium salts could be isolated and were found to be stable even at room temperature. These ions act as alkylating agents and were used in related studies as precursors for generation of dialkyloxonium methylides. [(Trimethylsilyl)methyl]halonium ions could be prepared and studied only at low temperature (−78 °C). Raising the temperature and attempting to isolate the halonium ions cause disproportionation. The [(trimethylsilyl)methyl]halonium ions were found to readily alkylate ethers at low temperature, but no trialkylsilylation was observed.

In recent years silylated reagents have gained extensive use in synthetic organic chemistry as well as in mechanistic and structural studies. In the area of silylated reactive intermediates it has been shown that carbocations containing β-(trialkylsilyl)methyl groups exhibit increased stability. This stabilization has been attributed to the strong inductive electron release by the β-trialkylsilyl groups as well as through hyperconjugation between the β Si–C bond and the empty p orbital of the carbocationic carbon.[2,3] Hyperconjugation (σ–π) has been shown in cases where the Si–C bond can achieve a transcoplanar arrangement with the empty 2p orbital of the carbocationic center.[4]

α-Silyl-substituted carbocations have been prepared under stable ion conditions and studied by ^{1}H as well as by ^{13}C and ^{29}Si NMR spectroscopy.[5,6] The ^{13}C NMR chemical shifts of α-silyl-substituted carbocations have been shown to be substantially deshielded as compared to their parent carbon analogues. This deshielding has been attributed to the somewhat bulkier trimethylsilyl group decreasing the necessary overlap for charge delocalization to occur. Previous experimental studies have shown that an α-trialkylsilyl substituent acts as a weak electron acceptor apparently due to hyperconjugation and as an electron donor due to its inductive effect.[7]

In contrast to α- and β-trialkylsilyl-substituted carbocations, silyl-substituted halonium and oxonium ions were yet unknown and present a different situation due to the absence of a vacant p orbital at the cationic center required for pπ–dπ hyperconjugation to occur.

Recently we reported the use of β-trimethylsilyl-substituted oxonium ions in the fluorine induced formation and study of reactive dimethyloxonium methylide.[8] In

$$(CH_3)_3SiCH_2O^+(CH_3)_2 \xrightarrow{F^-} (CH_3)_3SiF + [^-CH_2O^+(CH_3)_2]$$

an analogous manner the preparation of alkylhalonium methylides from β-(trimethylsilyl)halonium ions has been attempted.[9] To date, few details of the preparation and study of silylated oxonium and halonium ions have been reported.

In our continued study of onium ions we now report the preparation under stable ion conditions, reactivity, and NMR spectroscopic (^{1}H, ^{13}C, ^{29}Si) study of a series of α- and β-trialkylsilyl-substituted oxonium and halonium ions.

Results and Discussion

Methyl[(trimethylsilyl)methyl]halonium ions were prepared in a manner analogous to that previously used by

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Table I. NMR Chemical Shifts of β-(Trimethylsilyl)halonium Ions and Their Precursors

	^{1}H, ppm			^{13}C, ppm			
	$Si(CH_3)_3$	XCH_2Si	XCH_3	$Si(CH_3)_3$	$SiCH_2X$	XCH_3	^{29}Si, ppm
$(CH_3)_3SiCH_2Cl$				−3.4	30.3		3.5
$(CH_3)_3SiCH_2Cl^+CH_3$	0.32	4.32	4.32	4.5	58.9	51.6	5.7
$(CH_3)_3SiCH_2Br$				−2.4	17.4		2.3
$(CH_3)_3SiCH_2Br^+CH_3$	0.35	4.10	4.05	−4.1	50.0	39.7	5.9
$(CH_3)_3SiCH_2I$				−0.8	−11.9		2.3
$(CH_3)_3SiCH_2I^+CH_3$	0.22	3.40	3.40	−3.5	18.9	9.0	6.2

Olah and co-workers for the preparation of unsymmetrical dialkylhalonium ions.[10] This entails the alkylation of (trimethylsilyl)methyl halides with methyl fluoride–antimony pentafluoride in SO_2 solution at −78 °C.

$$(CH_3)_3SiCH_2X + CH_3OS^+OSbF_6^- \xrightarrow[-78\ ^\circ C]{SO_2} (CH_3)_3SiCH_2X^+CH_3Sb^-F_6$$

1, X = Cl
2, X = Br
3, X = I

Ions **1**–**3** were found to be stable at −78 °C and were characterized by NMR spectroscopy. Attempted isolation of the ions at room temperature led to disproportionation.

$$2(CH_3)_3SiCH_2X^+CH_3 \xrightarrow{\Delta} (CH_3)_3SiCH_2X^+CH_2Si(CH_3)_3 + CH_3X^+CH_3$$

X = Cl, Br, I

On the basis of the trend of the decomposition temperatures of the ions the order of their stability was found to be **3** > **2** > **1**. The ^{1}H, ^{13}C, and ^{29}Si NMR data of the ions are summarized in Table I.

The ^{1}H NMR spectra showing the expected multiplicities do not necessitate further discussion.

Although ^{29}Si NMR spectroscopy has become increasingly important in recent years, the factors influencing ^{29}Si chemical shifts are not yet well understood.[11] However, Ernst and co-workers have demonstrated a linear relationship between ^{29}Si chemical shifts and Hammett substituent constants within a series of trialkyl-substituted aromatic compounds.[12] This suggests that a relationship between charge density and ^{29}Si chemical shifts may exist between closely related systems. The ^{29}Si chemical shifts of the ions **1**–**3** are deshielded 2.2, 3.6, and 3.9 ppm from their precursors, respectively. The trend of increasing downfield shift appears to be due to magnetic influences resulting from the increase in size of the halides.

While ^{13}C NMR chemical shifts cannot directly reveal charge density, they are probably the most important tool used in the study of cations generated under stable ion conditions. Many factors are known to affect carbon chemical shifts; however, in closely related systems, the shielding or deshielding effects reflect the trend of charge distributions. The validity of this has been shown previously in several studies.[13] As can be seen from Table I, the NMR shifts of the methylene carbons of ions **1**, **2**, and **3** indicate that little charge is localized onto these carbons. The deshielding from their precursors [(chloro, (bromo, and (iodomethyl)trimethylsilanes] is 28.6, 32.6, and 30.8 ppm, respectively. This clearly shows that these carbons are remaining sp^3 hybridized with the deshielding effects due only to the neighboring positive charge influence. Thus most of the charge in the β-silylhalonium ions is located at the halogen centers.

The extent of deshielding observed in β-(silylmethyl)halonium ions from their precursors is consistent with the deshielding observed in dialkylhalonium ions.[14] We have previously reported the trend of deshielding effects in dialkylhalonium ions including the deshielding of CH_2 carbons in methylethylhalonium ions from their precursors (ethyl chloride, bromide, and iodide), which are 33.5, 38.5, and 36.6 ppm, respectively. Comparison with presently studied ions **1**–**3** it can be concluded that the β-trimethylsilyl substituent does not stabilize the positive charge to any greater extent than alkyl substituents in the corresponding dialkylhalonium ions.

It is interesting to note that in the studied halonium ions the ^{13}C NMR shifts are increasingly deshielded for the homologous iodo, bromo, and chloro halonium ions, respectively. This is undoubtedly due to the increase in size of halogens accommodating more charge and to related magnetic shielding effects.

To study their chemical reactivity the ions **1**–**3** were mixed with dimethyl ether in SO_2 at −40 °C. The halonium ions rapidly methylated the dimethyl ether, giving trimethyloxonium ion. The reaction proceeds quantitatively with no formation of dimethyl[(trimethylsilyl)methyl]oxonium ion.

$$(CH_3)_3SiCH_2X^+CH_3SbF_6^- + CH_3OCH_3 \xrightarrow[-40\ ^\circ C]{SO_2} (CH_3)_3SiCH_2X + (CH_3)_3O^+SbF_6^-$$

Acidic β-[(trimethylsilyl)methyl]oxonium ions **4**–**6** were prepared by protonation of the corresponding alcohol or ether with HSO_3F–SbF_5 (magic acid) in SO_2/SO_2ClF at −78 °C. Upon allowing the solution to warm and evaporation of solvent these ions were stable and could be easily isolated at room temperature.

$$(CH_3)_3SiCH_2OR \xrightarrow[SO_2/SO_2ClF,\ -78\ ^\circ C]{HSO_3F\text{-}SbF_5} (CH_3)_3SiCH_2O^+HR$$

4, R = H
5, R = CH_3
6, R = $CH_2Si(CH_3)_3$

By alkylating methyl(trimethylsilyl)methyl ether with alkyl iodide/silver tetrafluoroborate[15] it was possible to prepare oxonium ions **7** and **8**.

$$(CH_3)_3SiCH_2OCH_3 \xrightarrow[CH_2Cl_2,\ \text{room temperature}]{RI/AgBF_4} (CH_3)_3SiCH_2O^+(CH_3)R$$

7, R = CH_3
8, R = C_2H_5

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Table II. NMR Chemical Shifts of β-(Trimethylsilyl)oxonium Ions and Their Precursors

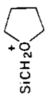
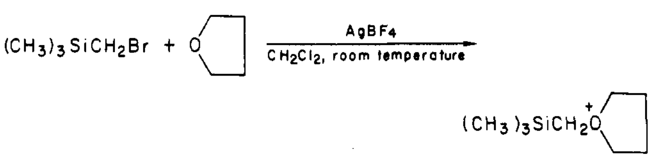
	^{1}H, ppm (J, Hz)						^{29}Si, ppm	^{13}C, ppm				
	$Si(CH_3)_3$	O^+-C-CH	$SiCH_2O^+$	$^+OCH_3$	$^+OCH_2-C$	^+OH		$Si(CH_3)_3$	$^+O-C-CH$	$SiCH_2O^+$	$^+OCH_3$	OCH_2-C
$(CH_3)_3SiCH_2OH$							−0.6	−3.6		56.0		
$(CH_3)_3SiCH_2O^+H_2$	0.06 (s)		4.40 (t, J = 3.6)			8.66 (t, J = 3.6)	1.1	−5.2		72.1		
$(CH_3)_3SiCH_2OCH_3$							−1.5	−3.2		67.6	63.3	
$(CH_3)_3SiCH_2O^+HCH_3$	0.05 (s)		4.25 (d, J = 4)	4.11 (d, J = 3)		8.32 (m)	0.4	−5.3		81.2	70.1	
$(CH_3)_3SiCH_2OCH_2Si(CH_3)_3$							−2.0	−3.1		70.2		
$(CH_3)_3SiCH_2O^+HCH_2Si(CH_3)_3$	0.38 (s)			5.20 (d, J = 3)		8.17 (q, J = 3)	0.2	−8.8		78.7		
$(CH_3)_3SiCH_2OCH_3$							−1.5	−3.2		67.6	63.3	
$(CH_3)_3SiCH_2O^+(CH_3)_3$	0.10 (s)		4.40 (s)	4.14 (s)			0.3	−6.4		89.4	77.2	
$(CH_3)_3SiCH_2OCH_3$							−1.5	−3.2		67.6	63.3	
$(CH_3)_3SiCH_2O^+(CH_3)CH_2CH_3$	0.10 (s)	1.50 (t, J = 7)	4.50 (s)	4.26 (s)	4.68 (q, J = 7)		0.3	−3.3	11.4	87.5	75.2	92.7
	0.16 (s)	2.24 (m)	4.40 (s)		4.55 (m)		1.0	4.3	23.8	84.3		86.0

Table III. ^{13}C Chemical Shifts (ppm) of Alkyloxonium Ions and Their Precursors[a,b]

	CH_3CH_2O	CH_3CH_2O	OCH_3
CH_3CH_2OH	57.3	17.9	
$CH_3CH_2O^+H_2$	76.3	13.6	
$CH_3CH_2OCH_3$	67.9	15.0	58.2
$CH_3CH_2O^+HCH_3$	83.4	12.5	66.3
$CH_3CH_2OCH_2CH_3$	67.4	17.1	
$(CH_3CH_2)_2O^+H$	80.5	12.8	
$CH_3CH_2OCH_3$	67.9	15.0	58.2
$(CH_3)_2O^+CH_2CH_3$	82.8	12.8	66.3
$CH_3CH_2OCH_3$	67.9	15.0	58.2
$(CH_3CH_2)_2O^+CH_3$	80.1	13.2	61.6
$(CH_3)_2O$			59.4
$(CH_3)_2O^+H$			69.9
$(CH_3)_2O$			59.4
$(CH_3)_3O^+$			79.3

[a] Oxonium ions were prepared as described previously by protonating alcohols[18a] or ethers[18b] or alkylating ethers.[18c,d] [b] Acidic oxonium ion spectra were obtained in FSO_3H-SbF_5/SO_2 solution at −70 °C and those of tertiary oxonium ions in SO_2 solution.

The alkylation of tetrahydrofuran with (bromomethyl)trimethylsilane/$AgBF_4$ in CH_2Cl_2 at room temperature led to preparation of ion **9**. After removal of silver halide the oxonium salts **7–9** were stable and could be even isolated at room temperature, although no further study of the salts was yet carried out.



9

The ^{1}H, ^{29}Si, and ^{13}C chemical shifts of ions **4–9** in methylene chloride/SO_2 solutions are shown in Table II. The ^{1}H data are straightforward and do not require further discussion. The ^{29}Si downfield shifts of ions **4–8** from their precursors are 1.7, 1.9, 2.2, 1.8, and 1.8 ppm, respectively. Thus the oxonium ion substituent [H, CH_3, C_2H_5, or $CH_2Si(CH_3)_3$] does not greatly influence the charge distribution at the β-silicon.

The ^{13}C NMR data of the oxonium ions can again be used to evaluate the extent of charge distribution and stabilization due to the β-trimethylsilyl substituent. As shown in Table II the deshielding of the methylene carbons of ions **4–8** from their parent precursors are 16.1, 13.6, 8.5, 21.8, and 19.9 ppm, respectively. This indicates that these methylene carbons are remaining sp^3 hybridized with little charge delocalization occurring. The observed deshielding can be attributed to the neighboring positive charge influence. The deshielding found in the ^{13}C NMR shifts of the β-(trimethylsilyl)oxonium ions from their precursors (see Table II) is similar to that observed for alkyloxonium ions. The ^{13}C NMR data for a comparable series of alkyloxonium ions are shown in Table III. As seen in Table III the deshielding of the methylene carbons for the analogous alkyloxonium ions are 19.0, 15.5, 13.1, 14.9, and 12.2 ppm. Thus, it can be concluded that the β-trimethylsilyl-substituent does not lead to significant charge delocalization in comparison to alkyl analogues. This is consistent with the previously discussed β-(trimethylsilyl)halonium ions.

Acidic α-trimethylsilyl-substituted oxonium ions **10–13** were prepared by protonation of the corresponding alcohol, ether, or siloxane in FSO_3H-SbF_5/SO_2 at −78 °C.

The ^{1}H, ^{29}Si, and ^{13}C NMR data for ions **10–13** are shown in Table IV. The ^{1}H chemical shifts showing expected multiplicities do not require further discussion. As

Table IV. NMR Chemical Shifts of α-Silyloxonium Ions and Their Precursors

	^{1}H, ppm (*J*, Hz)							^{29}Si, ppm		^{13}C, ppm					
	CHSi-$(\mathit{CH}_3)_3$	$^+$OSi-$(CH_3)_3$	CH_3CH_2-Si	$CH_3\mathit{CH}_2$-Si	$SiCH_2O^+$	$^+OCH_3$	^+OH	$(CH_3)_3$-SiC	$(CH_3)_3$-SiO$^+$	$(CH_3)_3$-SiO	$(\mathit{CH}_3)_3$-SiC	$SiCH_2O$	OCH_3	$CH_3\mathit{CH}_2$-Si	CH_3CH_2-Si
$(CH_3)_3SiOCH_3$									19.1	−1.4			49.7		
$(CH_3)_3SiOHCH_3$		0.67 (s)				4.20 (d, *J* = 4.5)	6.1 (q, *J* = 4.5)		61.9	−1.8			60.5		
$(CH_3)_3SiCH_2OSi(CH_3)_3$								−0.6	7.3	1.9	−3.6	55.8			
$(CH_3)_3SiCH_2O^+HSi(CH_3)_3$	0.45 (s)	0.80 (s)			4.40 (d, *J* = 5)		7.37 (t, *J* = 5)	0.9	49.9	−2.5	−5.8	68.0			
$(CH_3)_3SiOSi(CH_3)_3$									7.0	1.9					
$(CH_3)_3SiO^+HSi(CH_3)_3$		0.76 (s)					7.26 (s)	22.9	−2.0						
$(CH_3CH_2)_3SiOH$									18.5					5.7	6.5
$(CH_3CH_2)_3SiOH_2^+$			1.15 (s)	1.15 (s)			10.7 (s)	51.3						2.7	4.1
$(CH_3)_3SiOCH_3$									19.1	−1.4			49.7		
$(CH_3)_3SiO^+(CH_3)_2$		0.64 (s)				4.15 (s)			52.3	−1.3			60.5		

$$(R^1)_3SiOR^2 \xrightarrow[SO_2/-78\ ^\circ C]{HSO_3F\text{-}SbF_5} (R^1)_3SiO^+HR^2$$

10, $R^1 = CH_3$; $R^2 = CH_3$
11, $R^1 = CH_3$; $R^2 = CH_2Si(CH_3)_3$
12, $R^1 = CH_3$; $R^2 = Si(CH_3)_3$
13, $R^1 = CH_2CH_3$; $R^2 = H$

shown in Table IV the deshieldings of the ^{29}Si shifts range from 15.9 to 42.6 ppm. The magnitude of the ^{29}Si deshielding is apparently dependent upon the charge-delocalizing ability of the substituents. Ion **12** shows the smallest downfield shift probably due to a compensating effect between the two α-silyl substituents. The deshielding of the ^{13}C NMR shifts of the acidic α-(trimethylsilyl)oxonium ions from their precursors is slightly less than the deshielding observed for the analogous acidic alkyloxonium ions (see Table III). This is in sharp contrast to the extensive deshielding observed for α-silyl-substituted carbocations in which pπ–dπ hyperconjugation is significant as discussed above.[6] In α-(trimethylsilyl)oxonium ions **10–13** the trend of ^{13}C NMR chemical shifts indicates only a weak inductive effect the α-silyl group exerts upon the cationic center with very little or no additional charge delocalization occurring due to the trimethylsilyl group. Thus the inductive influence of a α-trimethylsilyl substituent is approximately as effective as that of a methyl substituent in stabilizing the cationic center. These results are also consistent with those obtained from theoretical studies.[16]

Attempted preparation of α-trimethylsilylhalonium ions via alkylation of the corresponding trimethylsilyl halides (chloride, bromide, iodide) using methyl fluoride/antimony pentafluoride in SO_2 at −78 °C led only to formation of α-trimethylsilyl fluoride through halide exchange.

Experimental Section

Material and Equipment. All silyl precursors were obtained from Petrarch Systems, Inc. or were prepared as reported elsewhere.[17]

^{1}H NMR spectra were recorded on a Varian A-56/60 spectrometer (δ, external Me_4Si). ^{13}C and ^{29}Si NMR spectra were recorded on a Varian FT-80 spectrometer. Chemical shifts are given from tetramethylsilane as reference (in case of ion spectra used as external capillary). Ion spectra, if otherwise not indicated, were obtained in SO_2 solution.

Methyl[(trimethylsilyl)methyl]halonium Ions. Solutions of the ions were prepared by adding the (trimethylsilyl)methyl halide in SO_2 at −78 °C to a solution of methyl fluoride/SbF_5 in SO_2 at −78 °C (1:1 mole ratio of β-silyl halide to SbF_5). After warming and evaporation of SO_2, disproportionation products were characterized by NMR.

Acidic [(Trimethylsilyl)methyl]oxonium Ions. Ions **4–6** were prepared by the dropwise addition of the corresponding alcohol or ether in SO_2 into FSO_3H–SbF_5 (1:1) in SO_2/SO_2ClF at −78 °C.

Dimethyl- and Methylethyl[(trimethylsilyl)methyl]oxonium Tetrafluoroborate. Methyl or ethyl iodide was added dropwise to a cooled solution (0 °C) of silver tetrafluoroborate and methyl(trimethylsilyl)methyl ether in dichloromethane (1:1:1 mole ratio of alkyl iodide to silver tetrafluoroborate to silyl ether). The mixture was stirred at room temperature for 2 h under exclusion of light and atmospheric moisture. The precipitated silver iodide was filtered off and the solvent removed under

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J. Org. Chem. **1985**, *50*, 4851–4855 **4851**

vacuum, yielding the oxonium salts which are stable at room temperature.

Tetramethylene[(trimethylsilyl)methyl]oxonium Tetrafluoroborate. A mixture of silver tetrafluoroborate, (trimethylsilyl)methyl bromide, and tetrahydrofuran (1:1:1 mole ratio) in dichloromethane was stirred for 3 days under exclusion of light and atmospheric moisture. The reaction mixture was worked up as described above.

Acidic (Trimethylsilyl)oxonium Ions. The ions **10**–**13** were prepared by the dropwise addition of the corresponding alcohol, ether, or siloxane in SO_2 into a FSO_3H–SbF_5 (1:1) solution in SO_2 at −78 °C.

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Registry No. **1**, 98704-62-2; **2**, 98704-64-4; **3**, 98704-66-6; **4**, 77871-44-4; **5**, 98704-67-7; **6**, 98719-89-2; **7**, 89909-23-9; **8**, 98704-68-8; **9**, 89909-27-3; **10**, 98704-69-9; **11**, 98704-70-2; **12**, 98704-71-3; **13**, 98704-72-4; $(CH_3)_3SiO^+(CH_3)_2$, 80754-55-8; $(CH_3)_3SiCH_2Cl$, 2344-80-1; $(CH_3)_3SiCH_2Br$, 18243-41-9; $(CH_3)_3SiCH_2I$, 4206-67-1; $(CH_3)_3SiCH_2OH$, 3219-63-4; $(CH_3)_3SiCH_2OCH_3$, 14704-14-4; $(CH_3)_3SiCH_2OCH_2Si(CH_3)_3$, 51264-54-1; CH_3I, 74-88-4; CH_3CH_2I, 75-03-6; THF, 109-99-9; $(CH_3)_3SiOCH_3$, 1825-61-2; $(CH_3)_3SiCH_2OSi(CH_3)_3$, 18297-68-2; $(CH_3)_3SiOSi(CH_3)_3$, 107-46-0; $(CH_3CH_2)_3SiOH$, 597-52-4; $CH_3CH_2O^+H_2$, 18639-79-7; $CH_3CH_2O^+HCH_3$, 52067-06-8; $(CH_3CH_2)_2O^+H$, 17009-83-5; $(CH_3)_2O^+CH_2CH_3$, 44209-06-5; $(CH_3CH_2)_2O^+CH_3$, 44387-70-4; $(CH_3)_2O^+H$, 17009-82-4; $(CH_3)_3O^+$, 43625-65-6; CH_3CH_2OH, 64-17-5; $CH_3CH_2OCH_3$, 540-67-0; $CH_3CH_2OCH_2CH_3$, 60-29-7; $(CH_3)_2O$, 115-10-6.

2-*endo*-[(Dimethylamino)methyl]-3-*endo*-(hydroxymethyl)bicyclo[2.2.1]hept-5-ene. A Model for Serine Esterases in the Aqueous Cleavage of *p*-Nitrophenyl Acetate

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The nucleophilic reactivity of the title amino alcohol (**1**) toward the carbonyl carbon of *p*-nitrophenyl acetate (PNPA) reveals the attack by both the free dimethylamino group and the internally hydrogen-bonded hydroxy group of **1**. The amino ester formed in the reaction of **1** with PNPA hydrolyzes ∼53 times faster than the ethyl acetate under essentially similar conditions. This enhanced reactivity is attributed to the probable intramolecular general acid-catalyzed expulsion of the leaving alkoxy group from the tetrahedral intermediate formed by the addition of hydroxide ion to the carbonyl carbon of amino ester. The reaction of **1** with PNPA giving the acetate of **1** as an intermediate and its subsequent enhanced hydrolysis to lose the acyl group again is taken as a model for the action of serine esterases.

There is strong evidence that the action of serine enzymes involves the attack on the carbonyl group of the substrate by the hydroxylic oxygen atom of a serine residue which has had its nucleophilicity increased by hydrogen bonding too and then proton transfer to an imidazole nitrogen atom from a histidine residue.[1-5] Jencks and Carriuolo[6] found that $(HOCH_2)_3CNH_2$ (TRIS) cleaves *p*-nitrophenyl acetate about $^1/_{15}$ as rapidly as *tert*-butylamine does although it is only about $^1/_{250}$ as basic. This was attributed to the nucleophilic attack largely by hydroxy groups on the basis of the observation that an intermediate, most likely an ester, was formed in the reaction. Bruice and York[7] studied the reaction of TRIS with aryl acetates, from which they got good Hammett equation correlations, with a ρ of 0.58 for the rate constant k_n for neutral TRIS and a ρ of 0.55 for the hydroxide ion catalyzed reaction. Although these values are much smaller than those obtained for reactions with ammonia (1.8) or imidazole (1.7–1.9), these authors preferred the amino group as the position of greatest nucleophilicity toward acyl carbon. Hersey et al.[8] have recently presented spectral evidence for ester formation in the reaction of TRIS with activated carbonyl compound 4-*trans*-benzylidene-2-phenyloxazolin-5-one.

Page and Jencks[9] found that ethanolamine and 3-quinuclidinol reacted with acetylimidazole some five times as rapidly as amines of comparable basicity that lacked hydroxy groups. They explained these observations by proposing a mechanism that involved the nucleophilic attack by anionic oxygen of zwitterion form of the amino alcohol. Werber and Shalitin[10] studied the reactions of tertiary amino alcohols with active esters, and they appeared to be probably the first to estimate the extent of reaction via the zwitterion forms of their amino alcohols. In almost all the studies where the amino alcohols brought about the efficient cleavage of esters, it could not be determined whether this cleavage had occurred by the attack of only amino or hydroxy group or of both the groups. The present study was initiated with an aim to explore the possibility of the existence of the internally hydrogen-bonded form of the title alcohol by reacting it with *p*-nitrophenyl acetate. The detailed kinetic studies and the analysis of the observed data are described in this manuscript.

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